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FUSED SALT SYNTHESIS OF MATERIALS FOR IR (INFRARED)

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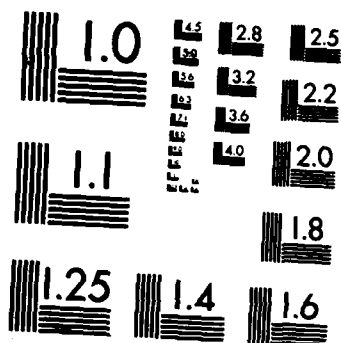
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# FUSED SALT SYNTHESIS OF MATERIALS FOR IR WINDOWS

TECHNICAL REPORT NO. 1

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Prepared for

Office of Naval Research  
800 N. Quincy Street  
Arlington, VA 22217-5000

P. Morgan  
M.S. Koutsoutis

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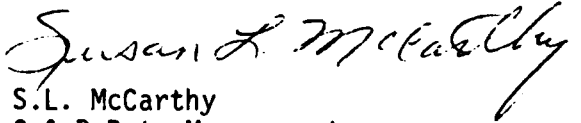
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The Technical Report No. 1 which was submitted to you on November 06, 1986, reflected incorrect information on the DD Form 1473. Enclosed you will find a "revised" copy of the Technical Report No. 1.

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## INTRODUCTION

Fused salt synthesis of a chalcogenide powder for infrared (IR) window use in the 8-12  $\mu\text{m}$  regime of the "atmospheric window" has been investigated. Materials for this application require erosion resistance, high hardness and strength with good thermal shock resistance. Oxides, with the required mechanical properties, because of their strong M-O bonds, especially when M is a light element, however, absorb in this region and a more massive anion is required.

As narrow bandgap materials will not fill the bill, especially at higher temperatures, one is left apparently with only the more ionic chalcogenides or pnictides. One considers, therefore, bonds such as Zn-Se, Ca-S, La-S, Zn-P, and a few others. The choices are few, as chalcogenide or pnictide bonds are less strong, leading to weaker and softer structures with higher thermal expansivity. Thermal expansivity in an approximately close-packed structure is proportional to individual bond valence.<sup>1</sup> Total strength can be related to total bond valence sum at the "cations and anions". The bonding requirements are therefore in conflict; strong bonds between light atoms are needed for mechanical properties, and weak bonds between heavier elements for IR transmittance. Compromise is the only solution.

Attempts at compromise have included  $\text{Zn}^{\text{IV}}\text{S}^{\text{IV}}\text{P}_2^{\text{IV}}$  (Wurtzite type)<sup>2</sup> (Roman numerals denote atom coordination). The idea here is to use low coordination with stronger bonds (to keep thermal expansion down). Unfortunately, the absorption edge is too low.<sup>3</sup> An alternative is to attempt to use many weaker bonds as in  $\text{Ca}^{\text{VIII}}\text{La}_2^{\text{VIII}}\text{S}_4^{\text{VI}}$  ( $\text{Th}_3\text{P}_4$  structure type),<sup>4,5</sup> however, the thermal expansivity is high as each bond valence is low.

One possible compromise, as discussed here, may be to use a six coordinated solid such as  $\text{Na}^{\text{VI}}\text{La}^{\text{VI}}\text{S}_2^{\text{VI}}$

For the 3-5  $\mu\text{m}$  "atmospheric window", various oxides and nitrides,  $\text{Y}_2\text{O}_3$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{AlN}$  and  $\text{AlON}$ , have been tried and sophisticated processing techniques<sup>6</sup> have been designed to fabricate them. This will be true for the 8-12  $\mu\text{m}$  candidates.

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It has become recognized that one efficient way of producing high-density, fine-grain oxide ceramics is to start with uniformly highly compacted monosize particles.<sup>7</sup> The aim is to achieve large numbers of particle-particle contacts, with uniform densification during sintering, so as to avoid the formation of large voids due to discontinuous effects,<sup>8</sup> this danger has been recognized for many years, but only recently studied in detail. Voids, especially larger ones, are sources of fracture initiation and light scattering. In the case of an IR window, if unavoidable pores can be kept below the size corresponding to the wavelength of interest, then transparency will be little affected. This should be easy for the 8-12  $\mu\text{m}$  regime of interest.

Less work has been done to produce chalcogenides of uniform particle size than for the case of oxides;<sup>9</sup> for complex mixed chalcogenides, new challenges are expected. A further advantage of carefully controlled growth of uniform particles should be improvements in purity of the product. This is especially important with respect to oxygen, ubiquitously property degrading, but unfortunately almost ever-present. It is anticipated that uniform particles of complex chalcogenides or other appropriate IR transparent materials should be readily fabricable into IR windows.

Many chalcogenides, due to their more covalent nature, and therefore lower bulk and grain boundary diffusion values relative to coarsening mechanisms such as evaporation-condensation, do not readily sinter<sup>10</sup> (if at all) and must be hot-pressed or HIPed (hot iso-pressed). It is extremely desirable to keep temperatures of fabrication low to avoid simultaneous grain coarsening, and hence mechanical weakening, and thus minimize evaporation-condensation and stoichiometry variation.

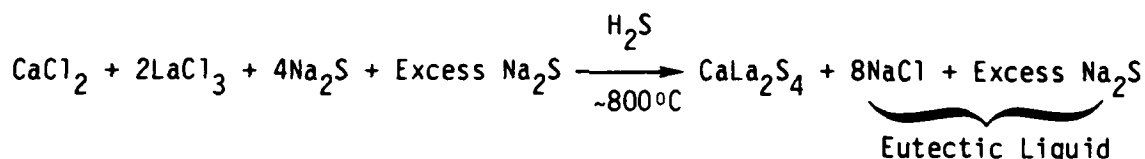
For this work, we have chosen the fused salt synthesis technique<sup>11-14</sup> for producing chalcogenides or pnictides with the aim of attaining controlled monosized particles in the 0.1-1  $\mu\text{m}$  size range. The fused salt technique promises to be a better method of attaining good stoichiometry with high impurity and low oxygen content, which has been a persistent problem.<sup>15</sup> This follows because the impurities and oxygen will tend to accumulate in the fused melt, while the particles are purified by solution-reprecipitation (Oswald ripening). The particles do not need to be milled (normally necessary to break up aggregates), thus eliminating a contaminating step. Initially, to establish the principles of the method, we attempted to use  $\text{CaLa}_2\text{S}_4$  as a prototype candidate. A surprise result led us instead to study  $\text{NaLaS}_2$ .



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## EXPERIMENTAL AND RESULTS

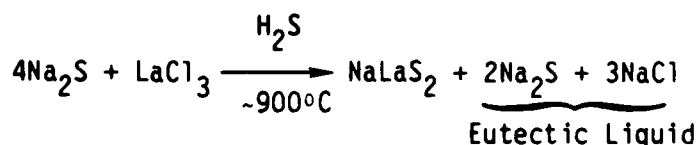
We wish to concentrate on cheap starting materials, potentially to be scaled up for later commercial use. We want the least number of steps to minimize labor, handling and contamination. Irreducibly simple, then, seemed to be the reaction in quartz inside a controlled atmosphere tube furnace:



With many tries, varying the ratios of the ingredients, surprisingly, no  $\text{CaLa}_2\text{S}_4$  was seen. Instead, recently discovered<sup>16</sup> rock salt structure  $\text{NaLaS}_2$  and  $\text{CaS}$  were the predominant products. Even more surprising to us was that when the by-product  $\text{NaCl} + \text{Na}_2\text{S}$  was extracted by solution in cold water, the  $\text{NaLaS}_2$  was not noticeably attacked. Contaminant  $\text{La}_2\text{O}_2\text{S}$ , present in the preparation and not produced by reaction with the water, was seen, suggesting a method of further lowering the oxygen potential, beyond that achievable by  $\text{H}_2\text{S}$ , was needed. It was further observed that, indeed, the  $\text{NaCl}-\text{Na}_2\text{S}$  eutectic was in the region of  $800^\circ\text{C}$  (the  $\text{NaCl}-\text{Na}_2\text{S}$  phase diagram has not been done!).

$\text{NaLaS}_2$  has the rock salt structure, i.e.,  $\overset{\text{VI}}{\text{Na}}\overset{\text{VI}}{\text{La}}\overset{\text{VI}}{\text{S}_2}$ ; thus, its six-fold coordinated structure may give usably low thermal expansivity while still having weak enough bonds for the absorption edge to be at a sufficiently long wavelength. In any event, it represented a new candidate for further study of the method.

The incredibly simple reaction:







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was used with the slightly higher temperature. Again,  $\text{La}_2\text{O}_2\text{S}$  appeared as a low-level impurity and varying ratios of ingredients did not remove it.

To reduce oxygen further, the test was redone in carbon disulfide vapor by bubbling argon gas through  $\text{CS}_2$  liquid. It was considered that this might produce some carbon deposits (it didn't), but even should they form with this method, the carbon would form floating on the fused salt, and thus be easily removed. It was found that by using a ratio of 2:1  $\text{Na}_2\text{S}:\text{LaCl}_3$ , almost pure  $\text{NaLaS}_2$  was achieved (< 5% of  $\text{La}_2\text{O}_2\text{S}$  remained). At this point, alternative extraction studies were commenced. It was found that ethanol effectively removed  $\text{NaCl}$  and  $\text{Na}_2\text{S}$  in a Soxhlet extraction under argon, but that the method was extremely slow with > 10 g amounts. If water was used for at least one day in a Soxhlet,  $\text{NaLaS}_2$  was decomposed (the water was ~ 60°C in this case).

Using a ratio of 2:1,  $\text{Na}_2\text{S}$  to  $\text{LaCl}_3$ , produced purer  $\text{NaLaS}_2$  with only a trace of  $\text{La}_2\text{O}_2\text{S}$  after 7 h under  $\text{CS}_2$ . If the mix was held for one day at 900°C in  $\text{CS}_2$ , then  $\text{La}_2\text{S}_3$  was a minor impurity.

At this point, another minor impurity was encountered whose presence increased with more excess  $\text{Na}_2\text{S}$  (desirable to produce a lower melting flux - easier to dissolve in organic solvents). It was found that the impurity could be isolated from the mixed  $\text{NaLaS}_2$ /impurity product by treating with cold acetic acid which dissolves  $\text{NaLaS}_2$ . The impurity was examined by energy dispersive x-ray fluorescence (EDS) which indicated La, Na (trace), Si and S. Material purified in this way was x-rayed; the diffraction pattern was analyzed by computer unit cell finders and turned out to be a (new) apatite structure,  $\approx \text{Na}_{0.5}\text{La}_{4.5}(\text{SiO}_4)_3\text{S}$ , hexagonal  $\text{P6}_3/\text{m}$ ,  $a = 9.911\text{\AA}$ ,  $c = 7.025\text{\AA}$ ,  $c/a = 0.709$ .

After heating in air to 1000°C, the apatite became more poorly crystalline with cell parameters:  $a = 9.874\text{\AA}$ ,  $c = 7.016\text{\AA}$  and  $c/a = 0.711$ . For the known  $\text{NaLa}_4(\text{SiO}_4)_3\text{F}$ :<sup>17</sup>  $a = 9.689\text{\AA}$ ,  $c = 7.1805\text{\AA}$  and  $c/a = 0.741$ . For a group of apatites,<sup>18</sup> it is known that the  $c/a$  ratio falls when the trigonal site in apatite, i.e., the F site in  $\text{NaLa}_4(\text{SiO}_4)_3\text{F}$ , is occupied by a larger anion such as Cl. In our case, the  $c/a$  ratio indicates that the detected sulfur is probably in this site, as suggested above. We believe this is the first known apatite of this type. Naturally, the finding of Si in the impurity suggested that  $\text{Na}_2\text{S}$ , especially in excess, was attacking the quartz containers used to



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contain the flux melt. We therefore switched to using carbon crucibles. At this point, no further impurity was seen, and the  $\text{Na}_2\text{S}$  content was conveniently increased to about 2:1  $\text{Na}_2\text{S}:\text{NaCl}$  in the flux.

Samples of  $\text{NaLaS}_2$ , which have been standing in ambient air for 14 months, still give XRD patterns that appear to be unchanged from the originals. However,  $\text{NaLaS}_2$  is attacked by hot water, so continuing studies have been carried out to remove the growth flux with organic solvents. We have found  $\text{C}_2\text{H}_5\text{OH}$  to be effective, but slow in a Soxhlet extraction. We now favor dimethyl formamide, DMF,  $\text{HCON}(\text{CH}_3)_2$  in a well thermally insulated system where the Soxhlet thimble is at about  $140^\circ\text{C}$ . A resulting preparation of x-ray pure  $\text{NaLaS}_2$  is shown in the accompanying photograph, where well-rounded  $10\text{ }\mu\text{m}$  "apples" of  $\text{NaLaS}_2$  are shown (the reason for the curious shape is unknown). To obtain the desired  $\approx 1\text{ }\mu\text{m}$  size spheres, we will have to go to much shorter times of Oswald ripening. This is an immediate future task.

As an example of the relative uniformity in  $\text{NaLaS}_2$  product, Figure 1 shows SEM pictures of the product at indicated magnifications after extraction of the eutectic melt with cold water. The slight surface "contaminant" may be due to reaction with the water.

### CONCLUSION

→ This type of very simple fused salt chemistry appears to be a viable approach to modern ceramic synthesis of monosize particles of complex sulfides or other chalcogenides. ↗

### ACKNOWLEDGEMENT

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Figure 1 SEM of particles of  $\text{NaLaS}_2$ .



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